SOME EFFECTS OF ALKALI SORPTION AND OXIDATION
ON THE BEHAVIOR OF A CORNSTARCH

by

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INTRODUCTION

The oxidation of starch may be approached from two completely different viewpoints. The first is that of the research chemist whose basic interests lie in the chemical constitution of starch and who uses oxidative methods as a key to the intricacies of the starch molecule. The other is that of the industrial starch chemist who uses oxidative techniques to modify the starch granule to suit it for certain industrial purposes. In the first case, the starch granule is degraded to chemical entities of determinable molecular structure, while the industrial starch chemist is interested primarily only in those relatively mild chemical or physical changes which will adapt the starch to a particular use.

Starches which are commercially oxidized resemble raw starch to the extent that they retain practically the same granular structure, show typical polarization crosses, are insoluble in cold water, and show characteristic color reactions with iodine. Unoxidized starches give heavy pastes or gels when heated with water, while oxidized starches, at equal concentrations, give thinner-bodied pastes, whose thickness depends upon the degree of oxidation.

The most frequently used oxidative reagents in the commercial oxidation of starch are sodium and calcium hypochlorites. This oxidation is brought about by the reduction of the positive valent chlorine in the sodium hypochlorite to the negative valent chlorine in sodium chloride, with subsequent release of one-half

mole of oxygen.

The general commercial method for producing hypochlorite oxi-
dized starches consists of treating aqueous starch suspensions
with a solution of hypochlorite which contains a slight excess of
alkali (3). The solution of hypochlorite is added in small por-
tions so that the generated heat can be absorbed by the cooling
system, the practice being to keep the temperature between 32° and
51° C. When the reaction appears to be approaching the desired
degree of oxidation, a sample of the starch milk is removed, fil-
tered, washed on a vacuum filter, and the viscosity of a paste of
definite concentration, prepared from the starch cake, is then
determined. When a paste of the desired viscosity is obtained,
the oxidation is stopped by adding an antichlor and the slurry is
adjusted to the desired pH, filtered, washed, and dried.

Industrial experience has indicated that the degree of oxi-
dation by the hypochlorite method given above is difficult to
control, and that the process would have greater industrial value
if some means for better control could be found. In working
toward this end, it was believed that more uniform oxidative ef-
fects would result by governing the uniformity of alkali sorption
with respect to sites, although there would be little basis for
anticipating that such effects would be more or less favorable
than those usually experienced.

It had been noted previously in this laboratory, that natural
cornstarch exhibits a considerable buffering action on both

acidic and basic solutions[1], and in doing so, a portion of the
acid or base might become sequestered within the starch granule.
Further, it was surmised that a portion of the sequestered acid
or base might become so sorbed, that it would be unavailable to
titration. A preliminary investigation involving the sorption of
sodium hydroxide by a starch slurry, revealed that some of the
buffering action by the starch was due to untitratable sodium
hydroxide which was sorbed by the starch granule. If these se-
questered sodium hydroxide molecules are sorbed at definite sites
on the starch granule, it seemed quite possible that, if chlorine
were added in the proper amounts, an oxidized starch would be ob-
tained which would meet the chosen requirements.

Therefore, the purpose of this investigation was to examine
the effects of the reaction of the untitratable sodium hydroxide
which was sorbed on a selected cornstarch with a determined amount
of chlorine.

SURVEY OF THE LITERATURE

The first observation of the oxidation of starch was recorded
by Justus Liebig in 1829 (Kerr, 4). He reported that starch is
slightly affected by the prolonged action of chlorine or chlorous
acid. In 1838, Pelouze determined that oxalic acid was one of the
products formed when starch was oxidized with concentrated nitric
acid (Kerr, 6). Haberman reported in 1874 the isolation of

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[1] Unpublished results.

gluconic acid from the products obtained by the oxidation of
starch with milder oxidative reagents, such as bromine water and
silver oxide (Kerr, 4). In 1891, Moissan reported that fluorine
attacks starch with the deposition of carbon (Kerr, 4). It was
noted in 1895 that a starch suspension, after a one-hour treatment
with bromine in sodium hydroxide, reduces Fehling solution, and
gives a slight precipitate with phenylhydrazine, while neither
bromine nor the alkali alone gives the effect (Kerr, 5). Follow-
ing these early developments were investigations on the oxidation
of starch by calcium and potassium permanganate, potassium
dichromate, hydrogen peroxide and ferric chloride, sodium perox-
ide, fluorine, manganese dioxide, perborates, persulfates, hypo-
chlorites, oxygen, and sodium p-toluenesulfonchloroamide (6).

EXPERIMENTAL

Preliminary Experiments

The term unimolecular layer is used throughout this paper to
define the amount of sodium hydroxide which is so sorbed by the
starch granule that it is not available to titration with hydro-
chloric acid. It is used in this manner to bring continuity
throughout the herein reported data. One unimolecular layer is
defined as that amount of sodium hydroxide required to cover,
with reference to the cross-sectional area of ionic sodium, a de-
fined amount of cornstarch having a specific surface of 3000
square centimeters per gram (2).

To determine that amount of normal sodium hydroxide solution required to form one unimolecular layer on 200 grams, dry weight, of cornstarch, the following procedure was used. Ionic sodium was used as the reference to determine the area that one sodium hydroxide molecule would occupy on the surface of the starch granule. The effective ionic radii of the sodium ion is 0.98×10^{-8} centimeters (8) and by using the formula for the area of a circle, πr^2, the effective area of the sodium ion was found to be 3.01×10^{-16} square centimeters. Since there are 6.02×10^{23} ions per mole, it was found that one gram-ion of sodium would occupy 18.1×10^7 square centimeters. By dividing the specific surface of starch, which is approximately 3000 square centimeters per gram, by 18.1×10^7 square centimeters per gram-ion of sodium, the value of 1.65×10^{-5} moles of sodium ion per gram of starch is obtained. Because of the approximations involved, the last figure derived was rounded off to 1.6×10^{-5}. Thus, by multiplying both sides by 200 and setting up the equality for a one normal sodium hydroxide solution, it was found that one unimolecular layer required 3.2 ml of one normal sodium hydroxide per 200 grams of starch (dry basis). This value was retained throughout this paper.

The starches used in this research were those of commercially prepared starches which were designated as CS-11 and CS-12 in this laboratory.

The effect of dilute alkali on a slurry of raw cornstarch was investigated by treating 200 grams, dry basis, of CS-11 slurried

in 700 ml of distilled water with 50 ml of normal sodium hydrox-
ide. Four samples were prepared as above and each was placed in
an open one-liter beaker and stirred for an arbitrary time of
forty-eight hours at the desired temperature. Temperatures of 45,
50, 55, and 60° C. were used, and from the data obtained it was
established that the amount of sorbed base, that is, that seques-
tered base which was not available to titration by hydrochloric
acid, increased with an increase in temperature. These alkali-
treated starches were labeled LP-02, LP-03, LP-04, and LP-05,
which correspond respectively to the temperatures of 55, 60, 45,
and 50° C.

To make a more quantitative study of the sorption of base by
starch, a one-liter, six-necked flask was constructed to insure an
enclosed system in which error from foreign elements would be
placed at a minimum. All fittings were made of ground glass
joints with the exception of two of the necks which were occupied
by the calomel cell and glass electrode connected to a Leeds and
Northrum pH indicator number 7664-AI. One of the ground glass
necks was used for a gas inlet diffuser, one for a gas outlet, one
for a thermometer, and the remaining neck for a stirrer which was
connected to a motor with a cone drive. This flask was placed in
a hot water bath in which the temperature was controlled by a
mercury switch thermostat.

The effect of dilute alkali on a cornstarch in an enclosed
system then was determined. Using the same concentrations as
given above, four samples of CS-12 were treated in an enclosed

atmosphere with nitrogen passing through the system at 40, 45, 50, and 55° C., respectively, for a period of 48 hours. Four other samples of CS-12 were prepared and treated the same as the four samples given above, with the exception that an oxygen atmosphere was used in place of nitrogen. At the end of the reaction time, the starch slurries were neutralized to pH seven with hydrochloric acid, and the amount of untitratable sodium hydroxide sorbed was calculated by the differences involved. The slurries were then washed, air dried, ground, and passed through a sixty mesh sieve. The nitrogen treated starches were labeled LP-16, LP-11, LP-21, and LP-13 to correspond, respectively, to the temperatures of 40, 45, 50, and 55° C.; and the oxygen treates starches were designated LP-33, LP-29, LP-30, and LP-31 to correspond, respectively, to the above temperatures. The data obtained from the above experiments, along with those of LP-02, LP-03, LP-04, and LP-05 are given in Table 1 in order to show the effects of varied conditions on the sorption of alkali by starch. It will be noted that, in the enclosed system, the amount of untitratable base sorbed is measurably less than that sorbed in the open atmosphere. It is assumed therefore that the carbon dioxide in the air was responsible for the major differences involved in the sorbed alkali of the two cases. It was noted that the samples treated under an atmosphere of oxygen sorbed slightly more alkali than the ones treated under an atmosphere of nitrogen, and that the untitratable base sorbed by the starch granule still increased with the temperature.

Table 1. Paste characteristics of starch products. (Preliminary experiments)

Starch product No.	Temp. in C.	u.m.l.* sorbed	W_1**	W_2***	$\dfrac{W_2}{W_1}$	G.S.**** in gms	$\dfrac{(G.S.-W_2)}{W_2(0.01)}$
LP-04	45	4.85	399	1461	3.66	1462	0.07
LP-05	50	5.93	336	1252	3.73	1075	-14.14
LP-02	55	5.97	296	1139	3.85	921	-19.14
LP-03	60	6.96	301	1140	3.79	866	-24.04
LP-16	40	1.42	----	----	----	---	-----
LP-11	45	1.64	----	----	----	---	-----
LP-21	50	2.47	---	----	----	---	-----
LP-13	55	3.80	---	----	----	---	-----
LP-33	40	0.91	428	1452	3.39	1137	-21.69
LP-29	45	1.87	453	1369	3.02	1348	- 1.53
LP-30	50	2.51	443	1352	3.05	1127	-16.65
LP-31	55	3.81	383	1209	3.16	1042	-13.81
LP-37	30	----	417	1226	2.94	2461	100.37
LP-35	30	----	598	1270	2.12	1543	21.50
LP-34	30	----	638	905	1.42	2029	124.20
LP-36	30	----	626	865	1.38	1625	87.86
LP-61	21	1.66	440	1249	2.84	1910	52.92
LP-59	45	1.89	448	1258	2.81	2368	88.20
LP-60	55	2.05	468	1244	2.66	1632	31.19

* NaOH sorbed in unimolecular layers.
** Hot paste viscosity in grams.
*** Cold paste viscosity in grams.
**** Gel strength in grams.

Viscosity measurements were run on LP-20, -30, -31, and -33 with a rotating-cylinder viscometer (1) which had been developed to measure continuously the changes in viscosity which take place in starch pastes throughout one or more cycles of temperature. The pasting curves obtained from the above-stated starches showed typical alkali-treated starch curves. Their pasting data are shown in Table 1.

It appeared, from the above experiments, that the unavailable sodium hydroxide which was sequestered by the cornstarch granule was sorbed at definite sites whose availability was defined by the prevailing experimental conditions. If the above assumptions are correct, then by adding free chlorine to neutral, alkali-treated starch suspensions, the added chlorine would react with the sorbed sodium hydroxide at those sites and thereby oxidize the starch in such a manner as to decrease the gross structure of the granule. It may be presumed that such structural changes are more uniform than those of industrial conversion, and that the extent of changes at or near the surface, as distinct from those which occur in depth, would govern the degree to which the starch will manifest glutinous behavior.

Samples of the alkali-treated starches LP-29, LP-31, and LP-33 were treated at room temperature for one hour with that amount of chlorine-water corresponding to a mole to mole reaction with reference to the untitratable sodium hydroxide sequestered by the starch granule. These oxidized cornstarches were then washed, filtered, air-dried, ground, and passed through a sixty-mesh sieve. Viscosity records of these starches were run on the above-mentioned viscometer and the starches were labeled LP-37, LP-35, LP-34, and LP-36 corresponding respectively to the temperature of 40, 45, 50, and 55° C. The viscosity records are shown in Fig. 1, and the data concerning the pastes are shown in Table 1. The pre-alkali treated, oxidized starches showed a more glutinous character than did the parent starch, but the pasting curves obtained
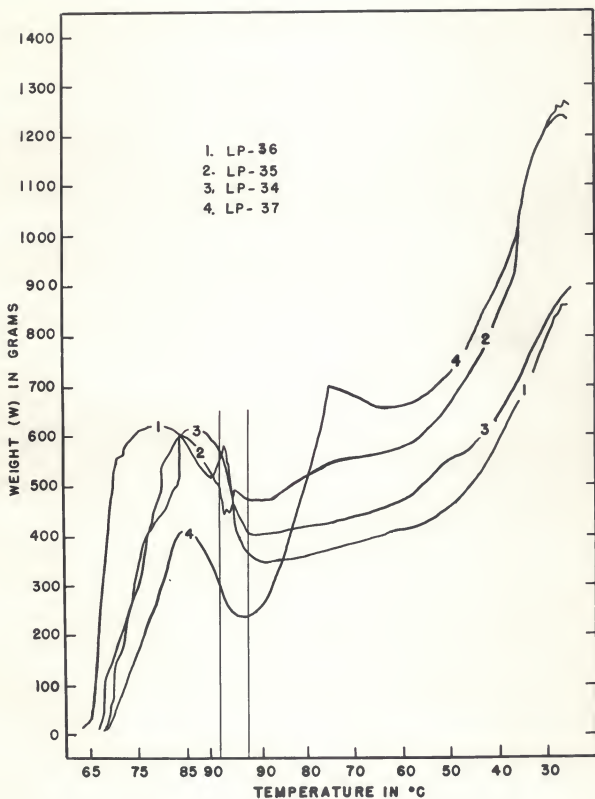
Fig. 1. Viscosity curves of starch products. (Preliminary experiments)

showed a certain degree of heterogeneity which denotes a non-
uniformity of reaction either within or among granules, or both.

The method for alkali sorption and oxidation thus far used
proved to be a long and tedious process, not giving desirable re-
sults as indicated by the heterogeneous character of the pasting
characteristics of resulting starches. It was suggested that a
shorter sorption period be used, to be followed directly by neu-
tralization and oxidation. If a series of shorter time periods,
defined approximately by the end of the period of rapid sorption,
were used instead of the long forty-eight hour sorption time, then
a more homogeneous reaction should occur on the surface of the
granule, thus producing a homogeneous pasting curve. The term
cycle, as used in this paper, comprises the sequence of changes
occurring during alkali sorption, neutralization, and oxidation.

As an approach to the time factor involved, four experiments
were run at 40, 45, 50, and 55° C., using an atmosphere of oxygen
for one complete cycle. A time vs pH plot was made for each tem-
perature, and the alkali sorption was stopped at the elbow of each
curve. The time of sorption ranged from two and one-half hours
for the 55° starch to five hours for the 40° starch. Viscosity
records were run on the four samples and it was found that both
the form of viscosity record and the characteristics of paste ob-
tained from the 55° starch showed it to have the most glutinous
character. This fact, together with the shorter time period used,
gave reason to select the 55° temperature for use in determining
more precisely the time periods that should be used for the
various cycles.

To further define the time factor, a six-cycle starch was prepared at 55 C., using an oxygen atmosphere. The first cycle had a two-hour alkali sorption period, and each succeeding cycle a one-hour sorption period. A time vs pH plot was made from the data of the above experiment and is shown in Fig. 2. It was decided from this graph that the sorption times could be decreased further to one hour during the first cycle, and to one-half hour during succeeding cycles. An eight-cycle starch was prepared using the same procedure that was used for the six-cycle starch, except for the use of the shorter sorption periods; the time vs pH plot also is shown in Fig. 2. The six-cycle starch was designated as LP-46 and the eight-cycle starch as LP-47.

Although the alkali sorption periods used in LP-47 were of the correct order of magnitude, the pastes obtained both from LP-46 and LP-47 possessed the properties of starches which had been treated with alkali alone, rather than those of oxidized starches; their pastes were cloudy and short. After consideration of these results, it was thought probable that, after so many cycles, the concentration of the salt formed by the reaction of chlorine and sodium hydroxide would be so great as to effectively block oxidation upon the addition of chlorine. To correct for this probable excessive salt concentration, the treated starches were washed between cycles in the remaining experiments until the filtrate showed no precipitate with a solution of silver nitrate.

In addition, two samples of starch were treated with a low concentration of sodium hydroxide, but due to the time factor in-
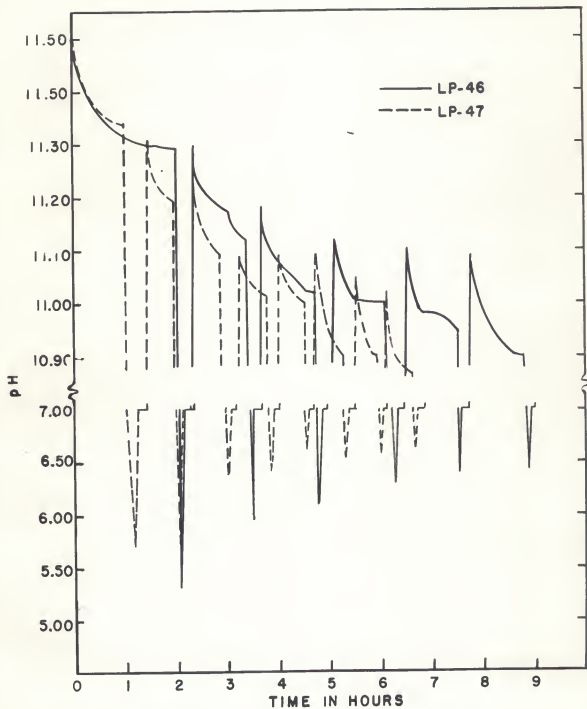
Fig. 2. Graphical representation of time factor in-
volved in preliminary experiments.

volved and the pastes obtained, the original concentration of 50
ml of one normal sodium hydroxide solution per 200 grams of starch,
dry basis, was found to be the most acceptable concentration for
the work at hand.

As was stated earlier in this paper, starches treated in the
presence of oxygen became slightly more glutinous compared to
those obtained in the presence of nitrogen. However, because the
use of oxygen would further complicate an already complicated
system, it was decided to use an inert atmosphere of nitrogen
throughout the remainder of the experiments.

To further define the temperature that should be used, three
oxidized starches were prepared using an atmosphere of nitrogen.
All three experiments consisted of three cycles using a one-hour
sorption period for the first cycle and one-half hour sorption
periods for the second and third cycles. Temperatures of 21, 45,
and 55° C. were used and the starches were designated as LP-61,
LP-59, and LP-60, respectively. All operations except the wash-
ing between cycles, were carried out at the designated tempera-
ture. Viscosity records were run on the above samples and the
pasting data are given in Table 1. The paste obtained from the
55° starch proved to be superior to the others, and for this
reason, together with experience obtained in the foregoing experi-
ments, 55° C. was chosen as the temperature to use in the final
experiments.

Final Experiments

For the first cycle of each of this series of experiments, a 150 gm quantity, dry basis, of CS-12 was slurried with 562 ml of distilled water and transferred to the six-necked flask mentioned earlier. The flask and its contents were then placed in a 55° C. water bath and fitted with a stirrer, thermometer, gas inlet diffuser, calomel cell, and a standardized glass electrode which was connected to a Leeds and Northrup pH indicator number 7664-AI. A cylinder of nitrogen gas was connected to the gas inlet diffuser, which was placed below the surface of the slurry, and nitrogen gas was allowed to bubble through the slurry for one hour, or until the slurry reached a pH of seven, to insure a system which was free from foreign elements. An atmosphere of nitrogen was retained throughout the experiment. After the system was cleaned, 37.50 ml of 0.9886 N sodium hydroxide was added dropwise to the slurry. The pH of the slurry was taken after the addition of the base and the drop in pH was followed on the pH indicator during all cycles. At the end of one hour's reaction time at 55° C., the alkali treated starch suspension was neutralized with normal hydrochloric acid to a pH of seven, and by the difference between the originally added base and the base corresponding to the added acid, the amount of sodium hydroxide unavailable for titration was calculated, which for the sake of clarity is designated as base A.

Saturated chlorine water at 30° C., prepared by passing chlorine gas through distilled water at this temperature, now was

added to the starch slurry in that amount which corresponds to a mole to mole reaction between the sequestered base and the chlorine. Upon addition of the chlorine water, the pH of the slurry immediately dropped to below pH seven and continued to drop slowly for the five minutes it was allowed to react in acid conditions. At the end of this five-minute period, normal sodium hydroxide solution was added to the slurry until a pH of seven was reached; this pH was maintained for five to ten minutes, depending upon the experimental requirements. The amount of base added during this period was noted and designated as base $\underline{B}$.

On completion of this oxidation process, the slurry was removed from the 55° C. water bath, filtered on a vacuum filter, and washed until the filtrate showed no precipitate with silver nitrate solution. When the washing process was complete, the starch cake was reslurried with 487 ml of distilled water, 75 ml of water being allowed for the water retained by the starch cake.

The slurry was then placed in the six-necked, one-liter flask and all connections made as before, and the flask and contents put in the 55° C. water bath, with nitrogen passing through the system. After reaching 55°, it was noted that the slurry was slightly alkaline. Normal hydrochloric acid was added until a pH of seven was reached, and that amount of base corresponding to the added acid was noted and designated as base $\underline{C}$. This point was the end of the first cycle.

For the second and succeeding cycles, 37.50 ml of 0.9986 N sodium hydroxide solution was added to the oxidized starch slurry,

the pH noted, and the slurry allowed to react for one-half hour
at 55° C. The slurry was then neutralized to pH seven with normal
hydrochloric acid solution, and the amount of base sorbed calcu-
lated as in the first cycle. This was designated as base $\underline{D}$. That
amount of chlorine water equivalent to (base $\underline{D}$ + base $\underline{B}$ - base $\underline{C}$ -
base $\underline{A}$) for a mole to mole reaction was then added to the slurry.
The reaction was allowed to take place under acid conditions for
five minutes, at which time the slurry was brought to pH seven
with normal sodium hydroxide solution and maintained at this pH
for five to ten minutes, depending upon the existing conditions.
After completion of oxidation, the slurry was removed from the hot
water bath and washed and reslurried as before. Again upon reach-
ing 55° C., it was noted that the slurry was alkaline; accordingly,
normal hydrochloric acid solution was added until pH seven was
reached. This ended the second cycle. In all the remaining
cycles the procedure followed was that of cycle two.

Samples of CS-12 were treated as given above from one through
13 cycles, with the exception of a twelve-cycle starch which was
not prepared. All of these cycled, oxidized cornstarches were
washed on a vacuum filter until the filtrate showed no precipitate
with a solution of silver nitrate, air dried at room temperature,
ground with mortar and pestle, passed through a sixty-mesh sieve,
bottled, and labeled. A 40-gram, dry basis, sample of each of
these oxidized starches was run on the viscometer, and carboxyl
groups were determined on each sample by the method given by Kerr
(7).

RESULTS AND DISCUSSION

As was given in the Final Experiments section, the base sorb-
ed during the sorption period of any one cycle was designated as
base $\underline{A}$, the base consumed in the back titration of acid formed
during the oxidation of that cycle as base $\underline{B}$, the alkali corres-
ponding to the acid added after washing as base $\underline{C}$, and the alkali
sorbed in the succeeding cycle as base $\underline{D}$. Further, it was stated
that chlorine water corresponding to a mole to mole reaction with
the sorbed alkali was added to (base $\underline{B}$ + base $\underline{D}$ - base $\underline{C}$ - base $\underline{A}$)
ml of base. In order to obtain a mole to mole reaction at those
sites on or within the granule at which the sodium hydroxide mol-
ecules were sorbed, base $\underline{A}$ should equal (base $\underline{B}$ - base $\underline{C}$). How-
ever, in many of the cycles run, (base $\underline{B}$ - base $\underline{C}$) was found to
be greater than base $\underline{A}$, which indicated that part of base $\underline{B}$ was
actually sorbed by the starch granule during the neutralization
after oxidation. In order to account for all the sorbed base,
that part of base $\underline{B}$ sorbed by the starch granule would have to be
added to the base sorbed during the succeeding cycle. Thus,
(base $\underline{B}$ - base $\underline{C}$ - base $\underline{A}$) ml was regarded as a part of base $\underline{D}$ in
the following cycle, and the equivalent amount of chlorine was
added to this amount of base during the following cycle. By using
the above procedure, a mole to mole primary reaction was obtained,
while the overall reaction is one in which two moles of sodium
hydroxide react with one mole of chlorine. As an example of the
above procedure, the data for the thirteen-cycle starch is shown
in Table 2. It will be apparent from the data of Table 2, that

the reaction proceeds as would be expected until about the seventh
cycle when the amount of base carried over to the next cycle begins
to increase very rapidly to a point where it exceeds that sorbed
during the sorption period. This was thought to be due to an in-
crease in the rupture of the lactone structure of the gluco-
pyranose unit by the sorbed sodium hydroxide molecules with the
subsequent formation of carboxyl groups through oxidation with
chlorine.

Table 2. Base consumed during successive cycles.

Cycle No.	Base B-C-A*	Base A	Total base**	Base B	Base C
1	----	1.68	1.68	2.74	0.70
2	0.36	1.70	2.06	2.74	0.68
3	----	1.91	1.91	2.47	0.64
4	----	1.90	1.90	2.25	0.43
5	----	1.80	1.80	2.30	0.45
6	----	1.75	1.75	2.45	0.31
7	0.39	1.55	1.94	2.60	0.34
8	0.34	1.50	1.84	2.70	0.34
9	0.52	1.63	2.15	3.10	0.31
10	0.64	1.57	2.21	4.22	0.40
11	1.61	2.42	4.03	7.75	0.50
12	3.22	3.24	6.46	11.51	0.40
13	4.65	4.30	8.95	15.40	0.42
--	6.43	----	----	-----	----

* This refers to the base carried over to the following cycle.
** This refers to the base given in the above discussion as
   (base B - base C - base A + base D).

To further clarify the supposed increase in carboxyl groups
with cycle number, carboxyl groups were determined on each sample.
The values obtained for the carboxyl groups are given in milli-
liters of 0.0098 N sodium hydroxide per gram of starch. They are

shown in Fig. 6 plotted against the cycle number. The graph shows a definite increase in the number of carboxyl groups after the eighth cycle with a period of uncertainty between the fifth and eighth cycles. Thus, the results point to the oxidation of the one-six lactone bond in the glucopyranose unit which becomes pronounced after the eighth cycle. This corresponds favorably to the data pertaining to alkali consumption. This effect is also shown in Figs. 3, 4, and 5.

The mechanism of the reaction was thought to proceed through the opening of the lactone structure of some of the glucopyranose units by sodium hydroxide molecules with the subsequent attack at these sites by chlorine and the formation of sodium chloride and organic hypochlorites. Due to the unstable character of the organic hypochlorites formed, hydrochloric acid would be released from the site of the reaction with the formation of a carboxyl group, and another mole of sodium chloride.

Upon examination of the pastes and pasting curves of the twelve oxidized starches, it appeared that a significant amount of oxidative degradation of the starch granule took place during the latter cycles; at least the alkali consumption of the starches increased rapidly after the eighth cycle and the viscosity decreased until a hot paste viscosity of zero was obtained (see Table 3 and Fig. 3). It was therefore conceived that new sites were available for attack by base during the first few cycles, but in the later cycles, the base repeatedly attacked the same regions in or on the granule, and literally bored holes into
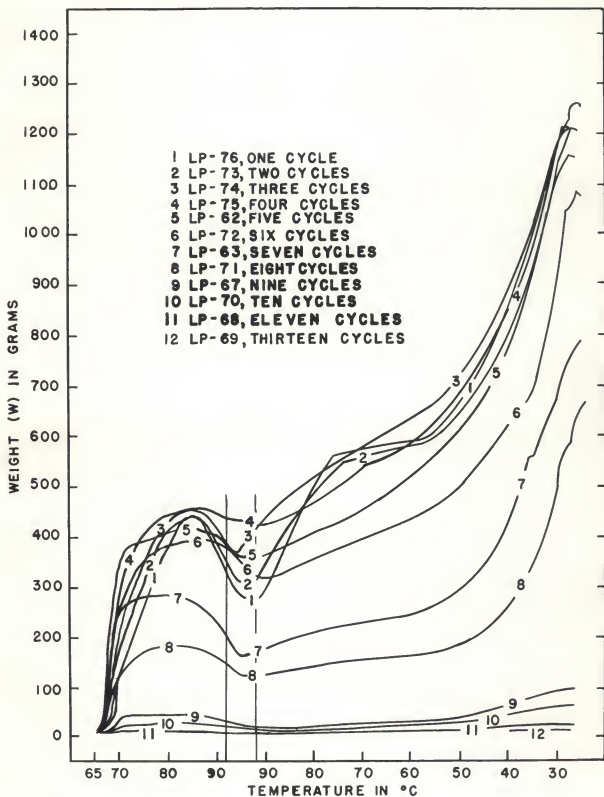
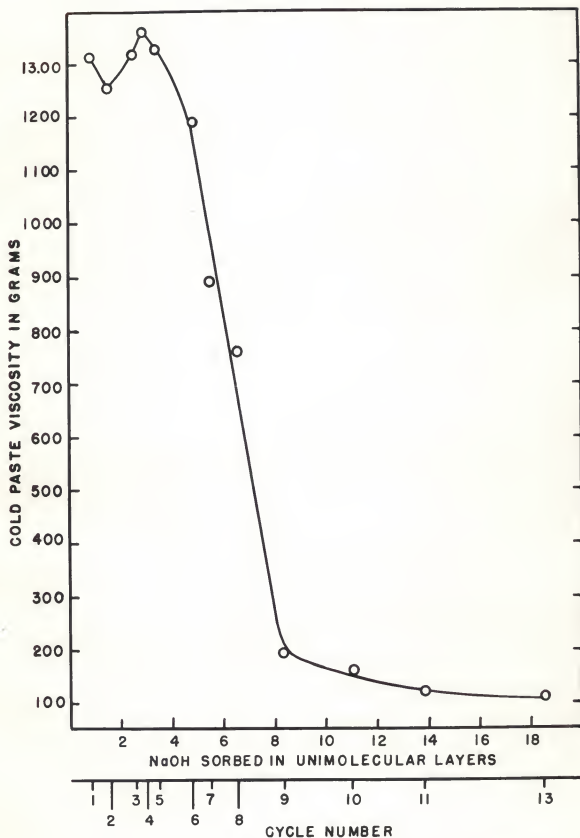Fig. 3.   Viscosity curves of starch products. (Final experiments)

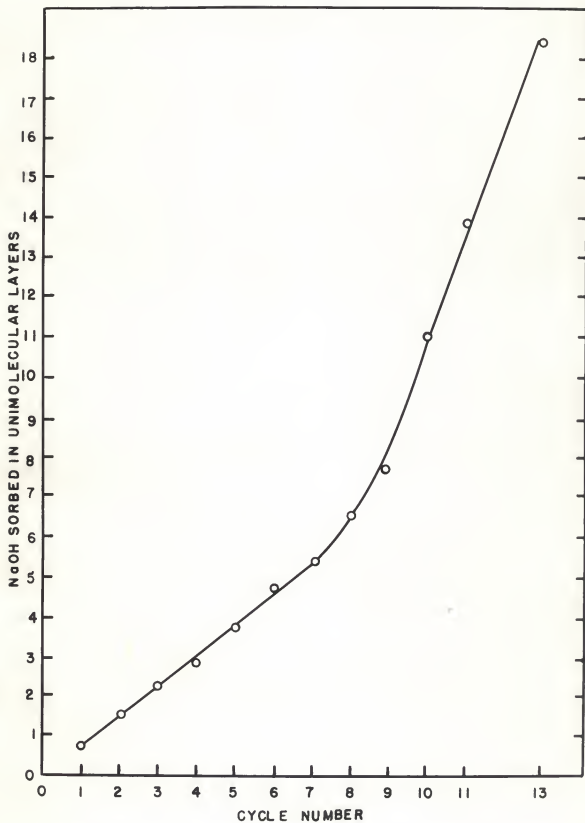Fig. 4. Effects of increasing amounts of untitratable NaOH on the cold paste viscosity.

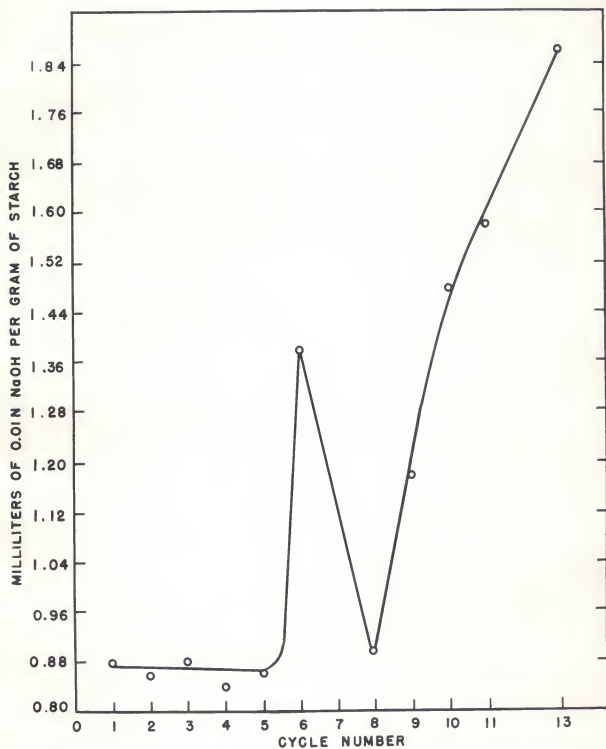Fig. 5. Effect of reaction rate with increase in cycle number.

Fig. 6. Effect of increasing amounts of untitratable NaOH on the carboxyl groups.

the granule causing the early surface effect to become an internal

effect.

Table 3. Paste characteristics of starch products. (Final Experiments)

Starch product No.	Cycle No.	u.m.l.* sorbed	W_1 **	W_2 ***	$\dfrac{W_2}{W_1}$	G.S.**** in gms	$\dfrac{(G.S.-W_2)}{W_2(0.01)}$
LP-76	1	0.78	444	1214	2.71	2284	88.14
LP-73	2	1.48	444	1158	2.61	1350	16.58
LP-74	3	2.25	457	1214	2.76	1524	25.54
LP-75	4	2.90	458	1262	2.76	1210	- 4.12
LP-62	5	3.74	417	1226	2.94	1249	1.88
LP-72	6	4.74	395	1094	2.77	1084	- 0.91
LP-63	7	5.35	285	791	2.78	1023	29.33
LP-71	8	6.56	183	666	3.97	782	17.42
LP-67	9	8.22	48	96	2.00	198	106.25
LP-70	10	11.03	24	62	2.58	120	93.55
LP-68	11	13.85	12	24	2.00	33	37.50
LP-69	13	18.41	0	9	0.00	9	00.00

   * NaOH sorbed in unimolecular layers.
  ** Hot paste viscosity in grams.
 *** Cold paste viscosity in grams.
**** Gel strength in grams.

From the data obtained, it appears that, in the main, the sodium hydroxide molecules continued their attack in the same regions of the granule during several cycles instead of attacking different sites in each cycle. If the latter effect had been obtained, starches making steady progress toward a more glutinous state should have been obtained; but as results turned out, starches were obtained whose pastes became increasingly thin-boiling and turbid. The thinness of the starch depended upon the degree of oxidation, while the clearness of the pastes increased during the early stages of oxidation, and then decreased. On the

whole, the pasting behavior of the series of starches was improved
through the fourth cycle but became progressively less desirable
thereafter. The results suggest that the temperature plays an im-
portant part in the internal structure of the granule. Thus, it
appears that the temperature may decrease the incidence of hydrogen
bonds, with the result that the internal structure may follow sur-
face changes during gelatinization and therefore, may swell with-
out rupture.

The pasting curves obtained from the twelve oxidized starches
in the final experiments indicate an increased effect of sorption
and oxidation between the eighth and ninth cycles. As can be seen
in Table 3 and Fig. 3, the drop in hot paste viscosity from the
first to eighth cycles was 261 grams, while the drop between the
eighth and ninth cycles was 135 grams, thus showing a definite
break in the degree of reaction after the eighth cycle. This
break is more clearly shown by the drop in cold paste viscosity;
the decrease was 548 grams between the first and eighth cycles and
570 grams between the eighth and ninth cycles. Figure 4 shows a
plot of the cold past viscosity in grams against the unimolecular
layers of base sorbed. It will be noted that, as the degree of
sorption and oxidation increase with cycle number, the cold paste
viscosity of the pastes drops rapidly. This effect is clearly
shown also when the cycle number is plotted against the number of
unimolecular layers of sodium hydroxide sorbed (Fig. 5). The
slope of the curve changes rapidly between the eighth and ninth
cycles. This indicates a highly increased reaction after the
eighth cycle with a more rapid formation of carboxyl groups as

shown in Fig. 6.

It appears, from the above data, that the reaction which took place at those regions on or in the granule, where sorption occurred, was too localized and severe to produce a mild reaction in which a gradual transformation could take place. Therefore, after the seventh to eighth cycle, a severe reaction occurred in which gross granular structure was retained, but the ability of the granule to retain water was lost.

It was noted that during the cooking period, the viscosity of the pastes increased from the first to the fourth cycle and decreased after the fourth cycle. This was true for the hot peak viscosity, while the cold paste viscosity varied irregularly for the first four cycles. It was noted also that the hump which appears in the pasting curve after the cooking period, which indicates structuralization, increases to a maximum in the third cycle and levels off after the fifth cycle.

While the quality of the pastes obtained was not increasingly improved, a procedure was found in which raw cornstarch could be oxidized in a controllable reaction. The pastes obtained from the first, second, third, and fourth cycle starches were fairly clear, heavy-bodied, and had a good gel strength, but with succeeding cycles, the pastes became increasingly thin-boiling and turbid (Table 3 and Fig. 3). Accordingly, the thirteen cycle starch paste was very thin-boiling and turbid with a hot paste viscosity of zero and a cold paste viscosity of nine. These highly oxidized starches apparently retained their gross granular structure, but lost their ability to retain water and to swell.

SUMMARY

A study was made of the effects of alkali sorption and sub-
sequent chlorine oxidation upon the behavior of a selected corn-
starch. It was thought that the alkali attacked the starch
granule, under the varied conditions given above, in such a man-
ner that the starch granule was left vulnerable to attack by
chlorine molecules in or on the granule. A method in which the
reaction could be controlled was sought and found. Although a
procedure was developed in which the degree of oxidation the
starch was to receive could be predetermined, the conditions used
in the Final Experiments were too severe to allow mild reactions
at the sites of reaction. The quality of the starch pastes pre-
pared increased through the fourth cycle, and then decreased.

It was shown that a primary reaction took place at the site
of reaction in which one mole of chlorine reacted with one mole of
sodium hydroxide with the formation of organic hypochlorites and
sodium chloride. The base added after oxidation to neutralize the
starch slurry gave an overall reaction of two moles of sodium
hydroxide with one mole of chlorine.

The determination of the carboxyl groups gave a reasonable
approximation to the extent of oxidation of the one-six lactone
bond in the glucopyranose units of some of the starch molecules.
These values determined, to a certain degree, the amount of
degradation occurring in the starch granule. The results obtained
were in complete agreement with the data pertaining to viscosity
measurements and alkali sorption.

ACKNOWLEDGMENTS

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SOME EFFECTS OF ALKALI SORPTION AND OXIDATION
ON THE BEHAVIOR OF A CORNSTARCH

by

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AN ABSTRACT OF A THESIS

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The purpose of this investigation was to examine the effects of the reaction of determined amounts of chlorine with untitratable sodium hydroxide which had been sorbed on a selected cornstarch.

After much preliminary work, the conditions for the final experiments were chosen. The temperature used was 55° C., with an enclosed atmosphere of nitrogen. Samples of raw cornstarch slurried in water were treated with chosen amounts of one normal sodium hydroxide to insure a system of approximately 0.065 normal sodium hydroxide solution. The above samples were placed in a specially constructed six-necked, one-liter flask which was placed in a hot water bath at 55° C. The various starch samples were allowed to react through over-all time periods which included those of alkali sorption, oxidation with chlorine, and neutralization; for sake of brevity, each over-all time interval was called a cycle. The time of alkali sorption was determined to be one hour during the first cycle and one-half hour for each succeeding cycle. The quantity of chlorine used and the time taken for oxidation in each cycle were dependent upon the amount of sodium hydroxide sorbed by the starch granules during the alkali sorption period.

Twelve samples of the untreated cornstarch were treated from one through 13 cycles, with the exception of a 12-cycle starch which was not prepared. Viscosity measurements were made on each of the twelve oxidized starches on a rotating-cylinder viscometer which was designed and built in this laboratory. Carboxyl group

determinations were made on each of the oxidized starches in order
to follow the degree of oxidation from cycle to cycle.

The pastes obtained from the twelve oxidized starch samples
made steady progress toward a more glutinous state up to the fifth
cycle where the pastes became increasingly thin-boiling and turbid
with increase in cycle number. The thinness of the paste depended
upon the degree of oxidation, while the clearness of the pastes
increased during the early stages of oxidation and then decreased.
Hence, a procedure was found in which raw cornstarch could be
oxidized in a reaction which could be controlled by the experi-
menter at all times; control could be obtained by reacting a
specified amount of chlorine with a calculated quantity of sodium
hydroxide molecules which were sorbed by the starch granules.

The reaction was thought to proceed through a mechanism in
which the lactone structure of some of the glucopyranose units in
the starch molecule were opened through attack by sodium hydrox-
ide molecules, with subsequent reaction at those regions or sites
by chlorine. The primary reaction at the above mentioned regions
or sites, was indicated to be a mole to mole relationship in re-
gard to the sorbed sodium hydroxide molecules and the added chlor-
ine, while the overall reaction showed two moles of sodium
hydroxide reacting with one mole of chlorine.

Alkali consumption by the starch samples followed a pattern
in which there was a sharp rise in alkali consumption after the
eighth cycle. This was explained through the assumption that the
sodium hydroxide molecules continued their attack in the same

region of the starch granule for several cycles instead of at-
tacking different sites each cycle. This was thought to be
especially true after the seventh to eighth cycle. The carboxyl
groups which were determined, indicated that the above assumption
was nearly true, for the values obtained for the carboxyl groups
remained nearly constant through the sixth to seventh cycle and
then rose sharply. This fact indicated a very definite increase
in the formation of carboxyl groups during the latter cycles, and
also, an increase in the rate of reaction during the sorption
period due to a weakening effect in the structure of the starch
granule after prolonged attack by sodium hydroxide molecules.